

Novel Sulfonated Poly(ether ether ketone ketone) Derived from Bisphenol S

Xianfeng Li, Hui Na, Hui Lu

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Jiefang Road 119, Changchun 130021, People's Republic of China

Received 30 June 2003; accepted 13 April 2004

DOI 10.1002/app.20861

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of sulfonated poly(ether ether ketone ketone)s derived from bisphenol S were prepared by nucleophilic polycondensation. They showed high thermal resistance and good solubility. Most of the polymers were easily cast into tough membranes. The swelling of the membranes (6.02–16.02%) was lower than that of Nafion membranes, and the ion-exchange capacity of the membranes

(0.67–1.44) was higher than that of Nafion membranes. The proton conductivity of the membranes was 0.022–0.125 S/cm. They could be used as proton-exchange membranes in fuel cells. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1569–1574, 2004

Key words: membranes; swelling

INTRODUCTION

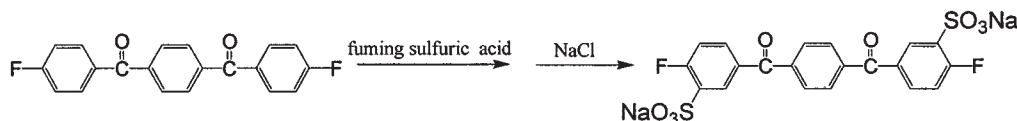
Fuel-cell technology is expected to become one of the key technologies of the 21st century for both stationary and dynamic applications, such as personal vehicles, trucks, buses, and locomotives, because fuel utilization in fuel-cell engines is markedly higher than in that combustion engines. Among fuel cells, proton-exchange-membrane fuel cells (PEMFCs) are the most promising power sources because they offer a highly efficient and environmentally friendly solution to energy conversion. The polymer electrolyte membrane (PEM) is the key component of a fuel-cell system because only highly stable membranes can withstand the harsh chemical and physical environment of a fuel cell, which includes chemically active noble metal catalysts in the fuel-cell electrodes, optional chemically aggressive fuels such as methanol and its partial oxidation products, aggressive oxidants such as oxygen, the formation of reactive radicals at the electrodes, especially at the cathode, and processing temperatures that can exceed 100°C.¹ The membranes traditionally used in PEMFCs are perfluorosulfonic polymers, such as Nafion from Dupont.² Although they show superior performance in fuel cells operating at moderate temperatures (<90°C) and high relative humidity with pure hydrogen as the fuel, the high cost, low conductivity at a low humidity or a high temperature,

and high methanol permeability has limited their use.³ The low conductivity at a low humidity or a high temperature and high methanol permeability of the membranes could reduce the cell efficiency. For this reason, many researchers hope to develop a high-performance and low-cost proton-conductive electrolyte membrane. Engineering thermoplastics such as polysulfones, poly(ether sulfone)s, poly(ether ketone)s (PEKs), and polyimides have been proposed as possible substitutes for perfluorinated ionomers. On this basis, new PEMs for fuel cells are being developed.

Poly(arylene ether ketone)s (PAEKs) are high-performance engineering thermoplastics. They have excellent mechanical properties and high thermooxidative stability. Thus, sulfonated PAEKs are interesting as PEMs. They have been prepared via a modification route, in which sulfonate groups are incorporated onto the polymer chains by a sulfonating agent^{4–8} such as concentrated sulfuric acid, complex sulfuric trioxide, chlorosulfuric acid, or methane sulfuric acid. An attractive alternative approach is the direct copolymerization of sulfonated PAEKs.^{9–12} The latter method is preferable to polymer modification because it is easy to control the degree of sulfonation through changes in the ratio of the sulfonated monomers and to avoid the side reactions associated with postsulfonation reactions. Poly(ether ether ketone ketone)s (PEEKs), members of the PAEK family, also have excellent properties, including especially good thermal stability and good mechanical properties, in comparison with PEKs. In this study, a series of sulfonated PEEKs with different concentrations of sodium sulfonate were prepared and researched.

Correspondence to: H. Na (huina@jlu.edu.cn).

Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 20320120169.



Scheme 1 Synthesis of the sulfonated monomer.

EXPERIMENTAL

Materials and measurement

1,4-Bi(4-fluorobenzoyl)benzene (applied by Longjing Chemical Plants, China) and bisphenol S (Yixing Chemical Plant, Jiangsu, China) were used as received. Potassium carbonate was dried at 180°C for 10 h before use. The other reagents and solvents were obtained commercially and used without further purification.

Synthesis of 1,4-bi(3-sodium sulfonate-4-fluorobenzoyl)benzene

A mixture of 1,4-bi(4-fluorobenzoyl)benzene (32.2 g, 0.1 mol) and 30% fuming sulfuric acid (50 mL) was heated at 110°C for 6 h. The solution was cooled and poured into ice water. The sulfonated compound was neutralized with sodium hydroxide and was precipitated with NaCl, filtered, and dried. The crude product was recrystallized from a mixture of methanol and water.

Yield: 43.6 g (83%). IR (KBr, cm^{-1}): 1656 (C=O), 1211, 1093, 621 (Ar—SO₃Na). ¹H-NMR [500 MHz, dimethyl sulfoxide (DMSO), ppm]: 8.12–8.15 (dd, 2.3 and 4.5 Hz), 7.87 (s), 7.81–7.84 (m, 2.5, 2.0, and 5.3 Hz), 7.34–7.38 (dd, 5.3 and 5.3 Hz). ¹³C-NMR (500 Hz, DMSO, ppm): 194.74, 163.34, 161.29, 141.01, 133.90, 132.81, 131.66, 130.29, 117.53.

Synthesis of sulfonated PEEKKs

To a 250-mL, three-necked flask equipped with a Dean–Stark trap, a reflux condenser, a nitrogen inlet, and a thermometer, bisphenol S, 1,4-bi(4-fluorobenzoyl)benzene (*k* mmol), 1,4-bi(3-sodium sulfonate-4-fluorobenzoyl)benzene (*m* mmol), dihydrous potassium carbonate, and DMSO were added. Toluene was used to remove the water which was produced in the reaction. The mixture was stirred at 140°C for 4 h and then raised to 170°C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed with water.

Analytical data for polymer c (*m* = 20 mmol, *k* = 20 mmol)

IR (KBr, cm^{-1}): 1080, 1240, 707 (Ar—SO₃Na), 1152 (—O—), 1651(C=O).

Analytical data for polymer e (*m* = 40 mmol, *k* = 0 mmol)

¹H-NMR (500 MHz, DMSO, ppm): 8.26–8.27, 7.90–7.98, 7.77–7.83, 7.20–7.22, 7.12–7.13. ¹³C-NMR (500 MHz, DMSO, ppm): 194.92, 162.25, 156.28, 141.10, 136.13, 133.43, 133.19, 131.81, 130.32, 122.69, 119.64.

Preparation of the membranes

Sulfonated PEEKK was first dissolved in dimethylformamide (DMF) to form a 5–10% solution, and the resulting mixture was cast onto a glass plate. Each membrane (50–100 μm) of the sulfonated polymer was prepared and dried at 85°C for 10 h and dried in a vacuum oven at 100°C for 48 h.

Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet Impact 410 FTIR spectrometer (USA), and ¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance 500 (Germany) with DMSO as the solvent and tetramethylsilane as the internal standard. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Netzsch STA449C (Germany) in air at a heating rate of 10°C/min. The proton conductivity at room temperature was measured by the four-probe method, and the resistance of the membranes was obtained from the slope of the U–V [voltage–current (U–I)] line; before the test, the membranes were immersed in water for 24 h.

The degree of swelling of sulfonated PEEKK (*S_w*) was determined from the difference in the weights of the drying membrane (*W_{drying}*) and the swollen membrane (*W_{wet}*). The drying membrane was weighed and then soaked in water until the weight remained constant. The membrane was then taken out and wiped with blotting paper, and it was weighed again. *S_w* was calculated as follows:

$$S_w = (W_{\text{wet}} - W_{\text{drying}}) / W_{\text{drying}} \times 100\% \quad (1)$$

The sulfonation degree of PEEKK is the number of sodium sulfonate group per repeating unit in the polymer chain. It was obtained by titration. Before titration, the polymer was acidified with an excess HCl solution, which transformed sodium sulfonate into sulfonated acid. The polymer in the sulfonated acid, which dissolved in DMF, was titrated with NaOH (0.01 mol/L), and the sulfonation degree was obtained.

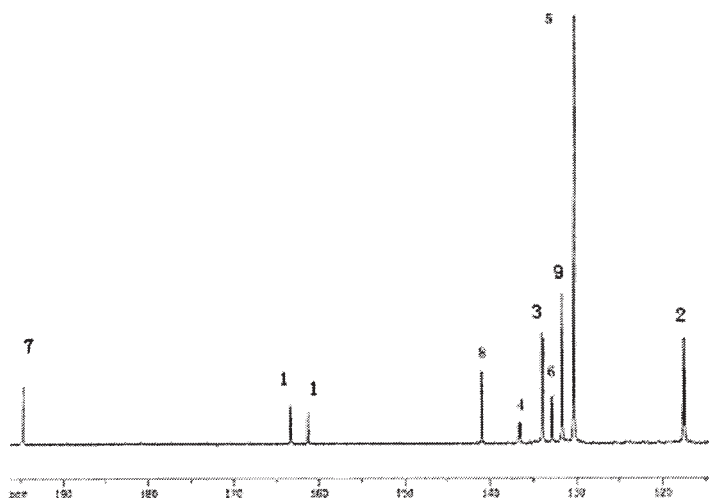
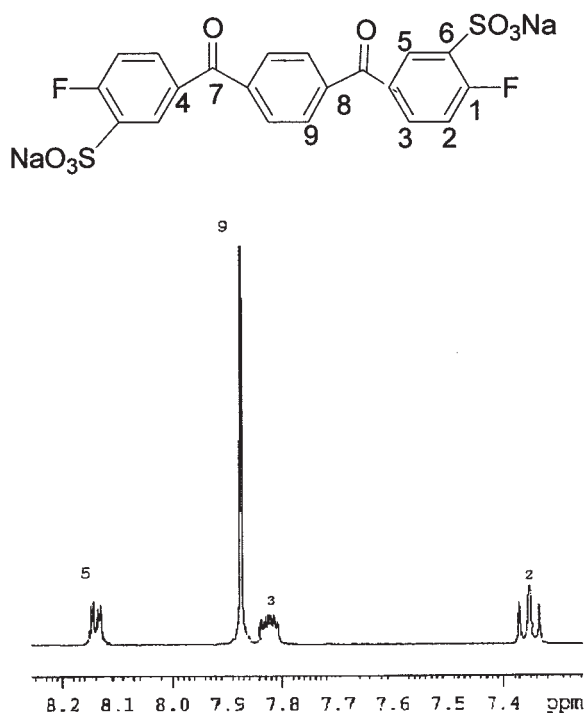


Figure 1 ^1H - and ^{13}C -NMR spectra of the sulfonated monomer.

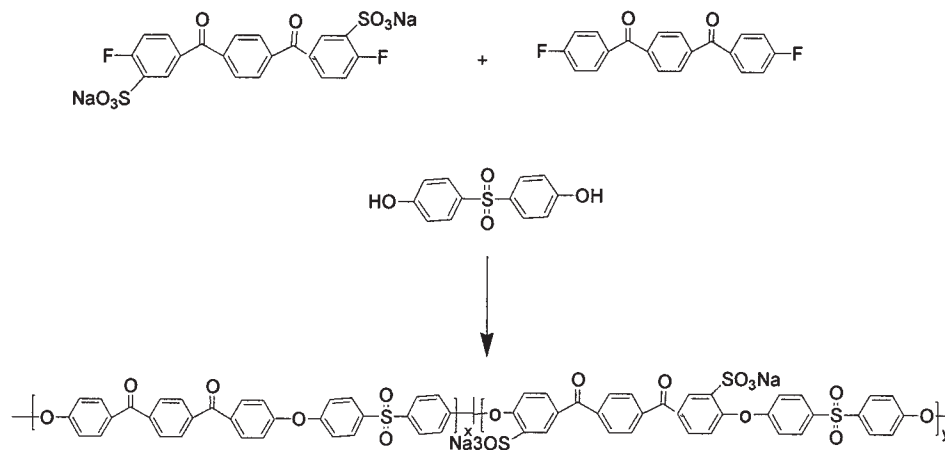
The ion-exchange capacity (IEC) of sulfonated PEEKK was determined by titration. The membranes in the H^+ form were immersed in a 1M NaCl solution for 24 h, and the H^+ ions in the membranes were replaced with Na^+ ions. The H^+ ions in the solution were then titrated with 0.01M NaOH. Then, the IEC of the polymer was obtained.

RESULTS AND DISCUSSION

Monomer synthesis

The sulfonated monomer, 1,4-bi(3-sodium sulfonate-4-fluorobenzoyl)benzene, was prepared via the sul-

fonation of 1,4-bi(4-fluorobenzoyl)benzene with fuming sulfuric acid (Scheme 1), followed by neutralization with NaOH and precipitation with NaCl. To control the polymer properties, we had to know the structure of the monomer. According to the electronic theory of orientation for electrophilic aromatic substitution, the sodium sulfonate groups were meta to the sulfonyl groups and ortho to the fluorine groups. The chemical structure of the monomer was determined with FTIR and ^1H - and ^{13}C -NMR. The IR spectrum of the monomer had $-\text{SO}_3\text{Na}$ at 1211, 1093, and 621 cm^{-1} and $\text{C}=\text{O}$ at 1656 cm^{-1} . The NMR spectra of the monomer are displayed in Figure 1, which indicates



Scheme 2 Preparation of polymers a–e.

the assignment of the peaks. All the results show that the monomer had the structure shown in Figure 1.

Polymer synthesis and characterization

Polymers with different degrees of sulfonation were prepared through the aromatic nucleophilic substitution polycondensation of bisphenol S with different ratios of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene to 1,4-bis(4-fluorobenzoyl)benzene (Scheme 2) in the DMSO/toluene solvent system, the temperature of the round flask was kept at 140°C for 3 h so that all the water could be azeotropically removed with toluene from the reaction mixture. The synthetic results and analytical data are displayed in Table I. The specific viscosities (>1.0 dL/g) of all the polymers showed that the sulfonated PEEKKs had high molecular weights. The sulfonation degree was determined by titration and indicated the successful synthesis of sulfonated PEEKKs.

The composition and structure of the sulfonated PEEKKs were confirmed with FTIR (Fig. 1) and ^1H - and ^{13}C -NMR (Fig. 2). Figure 1 shows the IR spectra of polymer c and PEEKK derived from bisphenol S. The absorption bands at 1240, 1080, and 1023 cm^{-1} were assigned to asymmetric and symmetric $\text{O}=\text{S}=\text{O}$

stretching vibrations of the sodium sulfonate groups. The absorption band at 707 cm^{-1} was assigned to the $\text{S}-\text{O}$ stretching of the sodium sulfonate groups. No peaks were attributed to the aromatic sulfone group in the range of 1140–1110 cm^{-1} ; this indicated that no crosslinking occurred during copolymerization. As for PEEKK, there was no related stretching for $-\text{SO}_3\text{Na}$. Absorptions at 1152 ($-\text{O}-$) and 1651 cm^{-1} ($\text{C}=\text{O}$) can also be found in Figure 2.

NMR spectroscopy was used to confirm the structure of polymer e. ^1H - and ^{13}C -NMR spectra and the peak assignments are shown in Figure 2 and were used to research the structure of the polymer chain. There were six peaks in the ^1H -NMR spectra of polymer e. The ^{13}C -NMR spectra of polymer e showed 13 peaks. This agreed with the structure of polymer e and indicated the structure of the polymers.

Properties of the sulfonated PEEKKs

Solubility of the sulfonated PEEKKs

The solubility of the polymers affected the preparation of the membranes and their properties. Table II presents the solubility of the sulfonated PEEKKs. All the polymers were easily dissolved in DMF, DMSO, and

TABLE I
Synthesis of the Sulfonated Polymers

Polymer	<i>m</i> (mmol)	<i>k</i> (mmol)	<i>m/k</i>	Yield (%)	$\eta_{\text{sp}}/c^{\text{a}}$	DS	$T_{10\% \text{ loss}}$ (°C)
a	8	32	2 : 8	94	1.23	0.48	525
b	16	24	4 : 6	93	1.34	0.90	495
c	20	20	5 : 5	95	1.40	1.05	492
d	24	16	6 : 4	93	1.22	1.31	310
e	40	0	10 : 0	94	1.22	1.72	439

m = 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene *k* = 1,4-bis(4-fluorobenzoyl)benzene; $T_{10\% \text{ loss}}$ = temperature for 10% weight loss; DS = sulfonation degree of the polymer.

^a Viscosity was measured at a concentration of 5.00 g/L in DMF at $25 \pm 0.1^\circ\text{C}$.

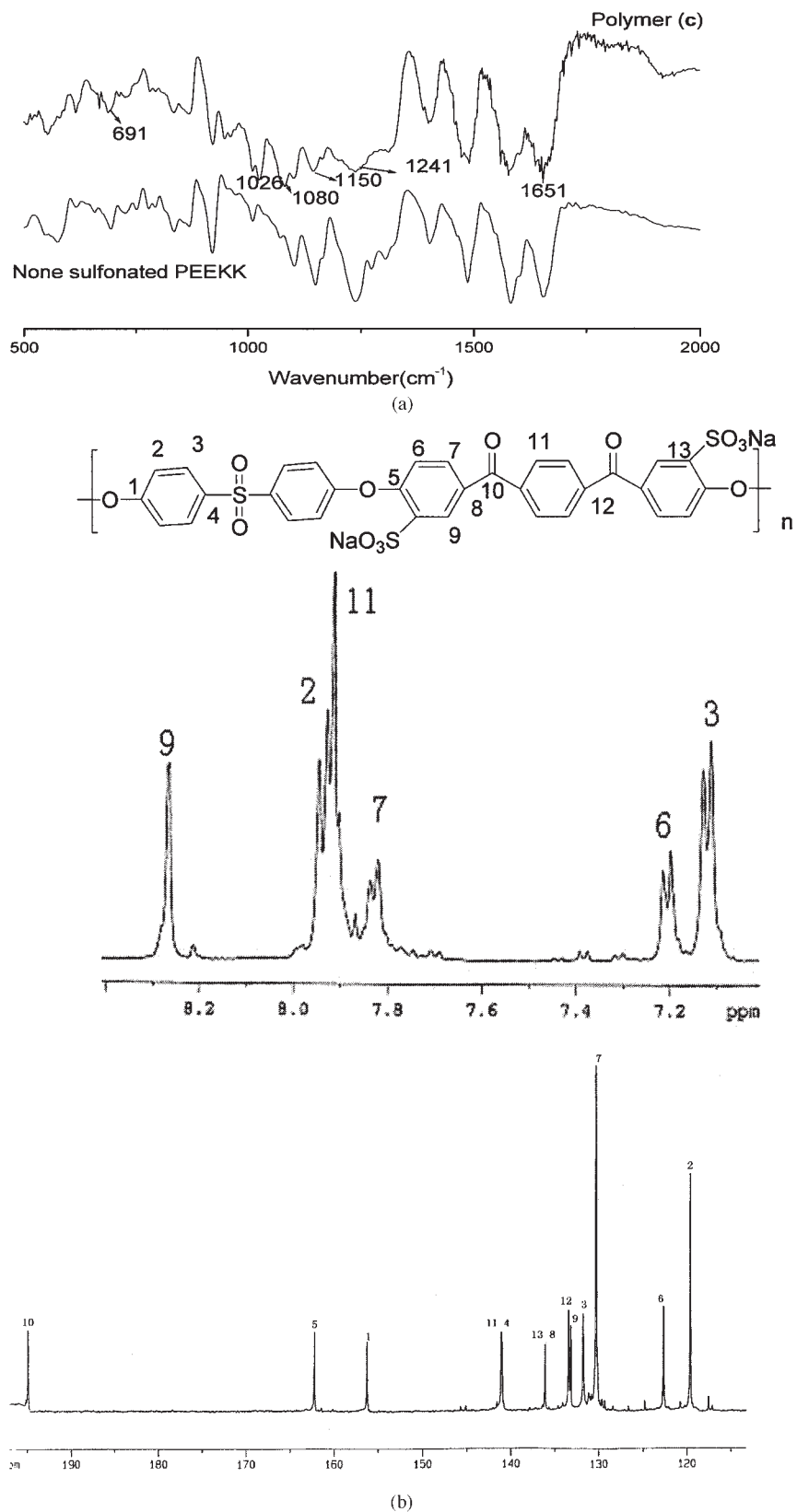


Figure 2 (a) FTIR spectra of polymer c and PEEKK and (b) ¹H- and ¹³C-NMR spectra of polymer e.

NMP (1-methyl-2-pyrrolidone). Polymer **e** was soluble in water at room temperature, and polymers **a–d** only slightly swelled in boiling water. Because of the presence of sodium sulfonate groups in the backbones of the polymers, there was strong solvation between water and the polymers. However, the solvation was not strong enough to cause polymers **a–d** to dissolve in water. This showed that the sodium sulfonate groups in the polymers had excellent hydrophilic properties. Because of the addition of $-\text{SO}_3\text{Na}$, the solubility of the sulfonated PEEKKs was better than that of PEEKKs in many solvents.

Thermal properties of the sulfonated PEEKKs

The thermal properties of the sulfonated PEEKKs were examined with TGA and DTA. No glass-transition temperatures and crystalline peaks were observed in the DTA curves of polymers **a–e** from 100 to 400°C. Therefore, they were amorphous polymers. From the TGA curves, we found that the temperatures of 10% weight loss for the sulfonated PEEKKs were all greater than 300°C (see Table I). This shows that the polymers had high thermal stability. We also found that the temperatures of 10% loss weight decreased with an increase in the concentration of sodium sulfonate groups in the polymer chain. This may be because the thermal decomposition temperature of the sodium sulfonate groups was lower than that of the backbones of the polymers.

Properties of the membranes

All the sulfonated PEEKKs were readily cast into tough membranes. The membranes were prepared through the dissolution of the polymers in DMF and were cast directly onto glass substrates. The membrane data are summarized in Table III.

The S_w and IEC values of the membranes increased with an increasing concentration of sodium sulfonate (Table III). Polymers **c** and **d** were soluble in water at

TABLE III
Properties of the Membranes

	Polymer				
	a	b	c	d	e
S_w	6.02	15.00	16.02	+	+
IEC (mequiv/g)	0.67	1.23	1.44	+	+
σ (s/cm)	0.02	0.07	0.12	+	+

σ = proton conductivity; + = soluble in water at room temperature.

room temperature, which could not be used for PEMFCs. S_w of the polymers was 6.02–16.02%. It was lower than that of Nafion 115 (34%). The IEC of the polymers (0.67–1.44) was much higher than that of Nafion 115 (0.91 mequiv/g). The sulfonated polymers showed excellent resistance to swelling. Furthermore, the conductivity of the sulfonated PEEKKs was 0.02–0.12 s/cm, an acceptable range for PEMs (>0.01 s/cm). The membranes showed very good potential for PEMFCs.

CONCLUSIONS

A series of sulfonated PEEKKs derived from bisphenol S were prepared by nucleophilic polycondensation. The chain structure of the polymers was confirmed with FTIR and NMR. They showed high thermal resistance and good solubility. The polymers were easily cast into tough membranes. S_w of the membranes (6.02–16.02%) was lower than that of Nafion membranes, and the IEC of the membranes (0.67–1.44) was higher than that of Nafion membranes. The proton conductivity of the membranes was 0.02–0.12 s/cm, a range acceptable for PEMFCs. They showed very good potential as fuel-cell membranes.

References

- Kerres, J. A. *J Membr Sci* 2001, 185, 3.
- Grot, W. G. *Macromol Symp* 1994, 161, 82.
- Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. E. *Eur Polym J* 1985, 17, 4.
- Litter, M. I.; Marvel, C. S.; Xu, J. *J Appl Polym Sci* 1996, 60, 1231.
- Daoust, D.; Devaux, J.; Godard, P. *Polym Int* 2001, 50, 917.
- Daoust, D.; Devaux, J.; Godard, P. *Polym Int* 2001, 50, 925.
- Daoust, D.; Devaux, J.; Godard, P. *Polym Int* 2001, 50, 932.
- Liu, S. Z.; Wang, F.; Chen, T. L. *Macromol Rapid Commun* 2001, 22, 579.
- Wang, F.; Chen, T. L.; Xu, J. P. *Macromol Chem Phys* 1998, 199, 1421.
- Can, D. J.; Lu, S. Q.; Wang, Z. J. *Polym Int* 2001, 50, 812.
- Xiao, G. Y.; Sun, G. M.; Yan, D. Y. *Macromol Rapid Commun* 2002, 23, 488.
- Nunes, S. P.; Ruffmann, B.; Rikowski, E.; Vetter, S.; Richau, K. *J Membr Sci* 2002, 203, 215.

TABLE II
Solubility of the Polymers

Solvent	a	b	c	d	e	PEEKK
DMF	+	+	+	+	+	+h
DMSO	+	+	+	+	+	+h
NMP	+	+	+	+	+	+
Water	–	–	sw	sw	+	–
Chloroform	–	–	–	–	–	–
Acetone	–	–	–	–	–	–
Methanol	–	–	–	–	–	–
Ethanol	–	–	–	–	–	–

+ = soluble at room temperature; – = insoluble; sw = swelling; +h = soluble on heating.